DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/270,874 filed on February 26, 2001.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 26th day of March, 2002

Atsuko Ikeda

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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Jun TANAKA, et al.

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SUBMISSION OF VERIFIED ENGLISH LANGUAGE TRANSLATION

Commissioner for Patents
P.O. Box 1450
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Sir:

Applicants respectfully submit herewith the Verified English Language Translation (29 (twenty-nine) pages of specification) for the Provisional Application No. 60/270,874 filed in the Japanese language.

Respectfully submitted,

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[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

Photo-Functional Powder and Applications Thereof

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a material having a photocatalytic function and a photo-functional property such as ultraviolet absorbing ability and transparency. More specifically, the present invention relates to a photo-functional powder, a slurry thereof and applications using the powder or slurry particularly by way of coating on the surface of fiber, paper or plastic or kneading into fiber or plastic or in the form of a coating material, such as polymer composition, coating agent, photo-functional formed article and photo-functional structure.

[0002]

[Background Art]

Heretofore, titanium dioxide is being widely used as a white pigment because of its excellent hiding power and superior tinting strength. It is known that when the titanium oxide is processed into ultrafine particles having a fine particle size, it exhibits new optical properties different from conventional titanium dioxide pigments. Based on this knowledge, studies are being aggressively

made on titanium dioxide fine particles. For example, when the titanium oxide is worked into a particle size of approximately half (1/2) the visible light wavelength, the scattering effect thereof is extremely reduced, as a result, the titanium dioxide transmits visible light while exerting its excellent ultraviolet absorbing effect. By utilizing such optical properties, the titanium oxide is taken notice of as an ultraviolet absorber capable of transmitting visible light.

[0003]

On the other hand, when the titanium dioxide particle is worked into fine particles, the surface area is increased and the effect of surface surpasses the effect of bulk as a particle, as a result, the photocatalytic effect of titanium dioxide particle comes out outstandingly. The photocatalytic mechanism of titanium dioxide is considered to proceed based on the following mechanism. First, when light is irradiated on the titanium dioxide fine particle, electrons and holes generated inside the titanium dioxide fine particle reacts with water or oxygen near the surface of the titanium dioxide fine particle to produce hydroxy radicals or hydrogen peroxide and by a strong oxidation-reduction action of this hydroxyl radical and hydrogen peroxide, harmful organic substances are purified into carbon dioxide gas and water. Such a photocatalytic action

of titanium dioxide fine particle is said to permanently continue insofar as titanium dioxide fine particle, light, water and oxygen are present. Using such photo-functional activity of titanium dioxide ultrafine particle, studies are being made on environmental purification such as antibiosis, deodorization, antifouling, air cleaning and water cleaning.

[0004]

With an attempt to utilize such a photo-functional activity of titanium dioxide fine particle, a method of kneading titanium dioxide fine particles into an easily handleable medium such as fiber and plastic formed article, or coating the fine particles on the surface of a substrate such as cloth and paper has been proposed. However, not only harmful organic substances or environmental contaminants but also the medium itself such as fiber, plastic and paper are easily decomposed and deteriorated by the strong photocatalytic activity of titanium dioxide and this stands as an obstacle to the practical use in view of durability. Also, because of easy handleability of titanium dioxide fine particle, a coating material prepared by mixing titanium dioxide fine particles and a binder has been developed, however, a binder satisfying the durability sufficiently high to overcome the problem (obstacle) of activity on the medium has not yet been found out.

[0005]

As for the related technology, JP-A-9-225319 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") and JP-A-9-239277 disclose a technique of preventing and suppressing the deterioration of resin medium or binder due to the strong photocatalytic activity of titanium dioxide particles, where as means therefor, a method of mounting a photoinactive compound such as aluminum, silicon or zirconium on the surface of a titanium dioxide particle like archipelago with steric hindrance and thereby suppressing the photocatalytic activity is proposed. However, this method is disadvantageous in that since the photoinactive compound is supported in the island form, a portion subject to the strong photocatalytic activity of titanium dioxide is present at a specific site of the resin medium or binder.

[0006]

JP-A-10-244166 proposes photocatalytic titanium dioxide prepared by coating the surface of titanium dioxide with porous calcium phosphate. However, in this case, as a problem pointed out, the photocatalytic performance decreases due to the coating film, that is, the calcium phosphate layer.

[0007]

International Patent Publication WO99/33566 discloses

a titanium dioxide fine particle powder material where a porous calcium phosphate coating layer is formed at least on a part of the surface of a titanium dioxide fine particle and an anionic surfactant is present at the interface thereof.

With respect to a slurry containing titanium dioxide having photocatalytic activity, JP-A-11-335121 discloses an anatase-type titanium dioxide-containing slurry obtained by subjecting a titania sol solution, a titania gel form or a titania sol·gel mixture to a heat treatment and at the same time, a pressure treatment in a closed container, and then to dispersion using ultrasonic waves or stirring.

[0008]

JP-A-11-343426 discloses a photocatalytic coating material having excellent dispersion stability, which is a photocatalytic coating material containing titanium dioxide and silica sol in a solvent, where the titanium dioxide has a Raman spectrum peak in the range from 146 to 150 cm^{-1} and 95% by mass or more of the titanium oxide is occupied by anatase-type titanium dioxide.

Despite these related techniques, it is impossible to provide a photo-functional powder material or slurry capable of satisfying all of the photo-functional property and when used together with an organic material, the durability and the dispersion stability by an industrially

useful method.

[0009]

[Problems to be Solved by the Invention]

By taking account of these conventional techniques, the object of the present invention is to provide a photo-functional powder, a slurry thereof and applications thereof, which can ensure excellent dispersion stability without impairing the photo-functional property of titanium dioxide and can more enhance the utility in industry.

More specifically, the object of the present invention is to provide a photo-functional powder which exhibits excellent photo-functional property, high durability and good dispersion stability at the coating on the surface of fiber, paper or plastic material, at the kneading into such a material or on use for coating material compositions; a slurry containing the powder; and a polymer composition, a coating agent, a photo-functional formed article and a photo-functional structure each using the photo-functional powder or slurry.

[0010]

[Means to Solve the Problems]

As a result of extensive investigations to attain the above-described object, the present inventors have found that, surprisingly, when a condensed phosphate containing an alkaline earth metal (hereinafter simply referred to as

"a condensed phosphate") is allowed to be present on the surface of a titanium dioxide fine particle, the soluble condensed phosphate is firmly coupled with the titanium dioxide fine particle and hardly liberated from the surface of titanium dioxide fine particle in a medium such as binder or resin and thereby, the problems described above can be overcome. The present invention has been accomplished based on this finding.

It is not clearly known why a condensed phosphate is firmly coupled with titanium dioxide fine particle when a titanium dioxide fine particle, a condensed phosphate ion and an alkaline earth metal ion are present together, however, the alkaline earth metal ion is considered to play a role like a binder between the condensed phosphate ion and the titanium dioxide fine particle.

[0011]

The present invention provides a photo-functional powder, an aqueous slurry containing the photo-functional powder and as applications of the photo-functional powder or aqueous slurry, a coating agent, a photo-functional organic polymer composition, a coating material using the polymer composition, a compound, a masterbatch for various formed articles, a photo-functional formed article and a photo-functional structure, which are described below.

[0012]

1. A photo-functional powder comprising titanium dioxide having allowed to present on the surface thereof a condensed phosphate containing an alkaline earth metal.

2. The photo-functional powder as described in 1 above, wherein the titanium dioxide has a primary particle size of 0.001 to 0.1 μm.

3. The photo-functional powder as described in 1 or 2 above, wherein the titanium dioxide contains any one crystal form of anatase, rutile and brookite.

4. The photo-functional powder as described in 1 above, wherein the condensed phosphate is at least one member selected from the group consisting of polyphosphate, metaphosphate and ultraphosphate.

5. The photo-functional powder as described in 1 above, wherein the alkaline earth metal is Mg or Ca.

[0013]

6. An aqueous slurry comprising the photo-functional powder described in any one of 1 to 5 above.

7. The aqueous slurry as described in 6 above, wherein the aqueous slurry has a pH of 5 to 9.

8. A coating agent using the aqueous slurry described in 6 or 7 above.

9. An organic polymer composition comprising the photo-functional powder described in any one of 1 to 5

above.

10. The organic polymer composition as described in 9 above, wherein the concentration of the photo-functional powder in the organic polymer composition is from 0.01 to 80% by mass based on the total mass of the composition.

11. The organic polymer composition as described in 9 above, wherein the organic polymer of the organic polymer composition is at least one member selected from the group consisting of synthetic thermoplastic resin, synthetic thermosetting resin and natural resin.

[0014]

12. A coating material using the organic polymer composition described in 9 above.

13. A compound using the organic polymer composition described in 9 above.

14. A masterbatch for a formed article selected from fiber, film and plastic formed article, using the organic polymer composition described in 9 above containing the photo-functional powder in a high concentration.

15. A photo-functional formed article obtainable by forming the photo-functional powder-containing organic polymer composition described in 9 above.

16. The photo-functional formed article as described in 16 above, wherein the photo-functional formed article is a formed article selected from fiber, film and plastic

formed article.

17. A photo-functional structure having on the surface thereof the photo-functional powder described in any one of 1 to 5 above.

[0015]

[Mode for Carrying Out the Invention]

In the present invention, the photo function of titanium dioxide particle is an optical function noticeably brought out when the titanium dioxide particle is worked into fine particles, and indicates photocatalytic function, ultraviolet ray absorbing ability, transparency or the like. The titanium dioxide for use in the present invention is fundamentally sufficient if it has a photo-functional property such as photocatalytic function, ultraviolet ray absorbing ability or transparency, and the crystal form and the production process thereof are not particularly limited. For example, the titanium oxide may be a titanium dioxide fine particle obtained through a vapor phase reaction or a wet reaction starting from titanium halide, a titanium dioxide fine particle or a sol thereof obtained by the wet hydrolysis of a titanic acid solution, or a sintered product thereof.

[0016]

The titanium dioxide fine particle for use in the present invention is not limited on the crystal form as

described above and may have any crystal form of anatase, rutile and brookite or may be a mixed crystal fine particle containing these crystals.

[0017]

The titanium dioxide for use in the present invention preferably has an average primary particle size of 0.001 to 0.1 μm. If the average primary particle size is less than 0.001 μm, such particles are difficult to efficiently product and this is not practical, whereas if it exceeds 0.1 μm, the titanium dioxide is greatly reduced in the transparency or photocatalytic function.

[0018]

In the present invention, the condensed phosphate is a salt obtained by the dehydration condensation of ortho-phosphoric acid (H_3PO_4) and although not particularly limited, polyphosphate, metaphosphate and ultraphosphate are preferred. The condensed phosphate is usually present in the range of preferably from 0.01 to 50% by mass, more preferably from 0.1 to 20% by mass, based on the mass of titanium dioxide.

If the condensed phosphate is less than 0.01% by mass, the medium itself is worsened in the durability due to the photocatalytic effect of titanium dioxide on the medium such as plastic, paper and fiber, whereas if the condensed phosphate exceeds 50% by mass, this is disadvantageous in

view of profitability.

[0019]

The present invention is characterized in that an alkaline earth metal (e.g., Be, Mg, Ca, Sr, Ba, Ra) is present on the surface or at the interface of the condensed phosphate. This alkaline earth metal plays a role like a binder between the condensed phosphate and the titanium dioxide fine particle and provides an effect of preventing the liberation of condensed phosphate from the surface of the titanium dioxide. The alkaline earth metal used is not particularly limited but is preferably Mg or Ca. The alkaline earth metal is usually present in the range of preferably from 0.01 to 20% by mass, more preferably from 0.01 to 10% by mass, based on the mass of titanium dioxide. If the alkaline earth metal is less than 0.01% by mass, it fails in playing a role as a binder and the condensed phosphate is readily liberated in the medium, whereas if the alkaline earth metal exceeds 20% by mass, the photo-functional titanium dioxide fine particles used in the present invention suffer from poor dispersibility.

[0020]

With respect to the means for coating this condensed phosphate containing an alkaline earth metal on the surface of titanium dioxide, a method of adding a predetermined condensed phosphate to an aqueous slurry containing

titanium dioxide, thoroughly dispersing the mixture, adding an aqueous solution of alkaline earth chloride or the like, and ripening the solution may be employed.

[0021]

In the above-described photo-functional powder, a metal such as platinum, rhodium, ruthenium, palladium, silver, copper and zinc may be previously supported on the surface of the titanium dioxide fine particle. In such a case, the environmental purification activity of the titanium dioxide fine particle is more enhanced and also, bactericidal and algicidal activities are enhanced. The metal may be supported on the starting material titanium dioxide or a process of allowing the above-described metal to be supported may be integrated into the step of adding the condensed phosphate or alkaline earth metal.

[0022]

In the present invention, the aqueous slurry means a water dispersion where the titanium dioxide is a titanium dioxide mainly comprising a titanium dioxide fine particle and having a condensed phosphate on the surface thereof and an alkaline earth metal is present on the surface or at the interface of the condensed phosphate. This water dispersion may contain a hydrophilic organic solvent.

[0023]

The photo-functional powder content in the slurry is

not particularly limited and, for example, the content is preferably from 0.01 to 50% by mass, more preferably from 1 to 40% by mass. If the photo-functional powder content is less than 0.01% by mass, a sufficiently high photo-functional property cannot be obtained after the coating, whereas if it exceeds 50% by mass, not only a problem of thickening or the like arises but also this is disadvantageous in view of profitability.

The pH of the aqueous slurry is from 5 to 9, preferably from 6 to 8. If the pH is less than 5, the base material or the like is chemically oxidized or corroded, whereas if the pH exceeds 9, not only the base material or the like is chemically changed but also the use environment is adversely affected.

[0024]

A binder is arbitrarily added to this water dispersion (slurry) to obtain a coating agent and the obtained coating agent is applied on the surface of various structures which are described later, whereby a photo-functional structure can be produced.

The binder material for use in the present invention is not particularly limited and may be an organic binder or an inorganic binder. Specific examples of the organic binder include polyvinyl alcohol, melamine resin, urethane resin, celluloid, chitin, starch sheet, polyacrylamide and

acrylamide. Examples of the inorganic binder include zirconium compounds such as zirconium oxychloride, zirconium hydroxychloride, zirconium nitrate, zirconium sulfate, zirconium acetate, ammonium zirconium carbonate and zirconium propionate, silicon compounds such as silane alkoxide and silicate, and metal alkoxide of aluminum, titanium or the like.

[0025]

The amount of the binder added in the coating agent is preferably from 0.01 to 20% by mass, more preferably from 1 to 10% by mass. If the amount of the binder added is less than 0.01% by mass, a sufficiently high adhesive property may not be obtained after the coating, whereas if it exceeds 20% by mass, not only a problem of thickening or the like arises but also this is disadvantageous in view of profitability.

[0026]

The photo-functional powder of the present invention can be used as a composition by adding it to an organic polymer. Examples of the organic polymer which can be used include synthetic thermoplastic resin, synthetic thermosetting resin and natural resin. By virtue of the presence of the condensed phosphate and the alkaline earth metal, the organic polymer is not brought into direct contact with the photocatalytic active face (surface) of titanium

dioxide, so that the organic polymer itself as a medium can be free of decomposition and deterioration and therefore, the durability of the organic polymer can be enhanced.

[0027]

Specific examples of the organic polymer include polyolefins such as polyethylene, polypropylene and polystyrene, polyamides such as nylon 6, nylon 66 and aramid, polyesters such as polyethylene terephthalate and unsaturated polyester, polyvinyl chloride, polyvinylidene chloride, polyethylene oxide, polyethylene glycol, silicon resin, polyvinyl alcohol, polyacetal resin, polyacetate, ABS resin, epoxy resin, vinyl acetate resin, cellulose and cellulose derivatives such as rayon, urethane resin, polyurethane resin, polycarbonate resin, urea resin, fluororesin, polyvinylidene fluoride, phenol resin, celluloid, chitin, starch sheet, acrylic resin, melamine resin and alkyd resin.

[0028]

The organic polymer composition containing the photo-functional powder of the present invention can be used in the form of a coating material (coating composition), a compound (for example, resin composition containing the powder), a masterbatch for formed articles containing the photo-functional powder in a high concentration, or the like. The concentration of the photocatalytic powder in the

organic polymer composition is from 0.01 to 80% by mass, preferably from 1 to 50% by mass, based on the entire mass of the composition. Also, an adsorbent such as activated carbon and zeolite may be added to the organic polymer composition so as to enhance the effect of removing malodorous substances. In the present invention, a polymer formed article having photo-functional property can be obtained by forming the above-described polymer composition. Examples of the formed article from the composition include fiber, film and plastic formed articles.

[0029]

The organic polymer composition of the present invention has excellent durability and therefore, can be used as a coating composition for structures such as wall material, glass, signboard and concrete road/building. Furthermore, when the titanium dioxide photocatalytic powder of the present invention is surface treated, the powder and the organic polymer composition using the powder, which is coated on a structure (organic product) of paper, plastic, cloth or wood, or on the coating of a vehicle or the like, can fully exert their optical function without causing photocatalytic deterioration and destruction of the medium (structure or film).

[0030]

[Examples]

The present invention is described in detail below by referring to Examples, however, the present invention is not limited to these Examples.

[0031]

Example 1:

(Preparation of Photo-Functional Slurry)

50 L of pure water previously weighed was heated while stirring and kept at a temperature of 98°C. Thereto, 3.6 kg of an Aqueous Titanium Tetrachloride Solution (produced by Showa Titanium Co., Ltd.) was added dropwise over 60 minutes. After the dropwise addition, the obtained white suspension was passed through an electrodialyzer and adjusted to a pH of 5. A part of the thus-obtained photocatalytic slurry was sampled and the solid concentration was measured by a dry constant weight method and found to be 2% by mass. The dried powder was subjected to a structure analysis using an X-ray diffraction apparatus, as a result, the obtained powder was brookite-type titanium dioxide.

Subsequently, 1 kg of sodium metaphosphate (for food addition, produced by Taihei Chemical Industrial Co., Ltd.) was added to the titanium dioxide slurry obtained and thoroughly stirred until this was dispersed.

Thereafter, 200 g of calcium chloride (for food addition, produced by Tokuyama Corp.) was added to 2000 L of pure water previously weighed to prepare a calcium chloride solution.

The obtained sodium metaphosphate-containing titanium dioxide slurry and calcium chloride solution were mixed and kept at 40°C for 4 hours. At this time, the electric conductivity was 10,000 μS/cm.

The thus-obtained slurry was cleaned by filtration through a rotary filter press (manufactured by Kotobuki Engineering & Manufacturing Co., Ltd.) and thoroughly washed with water until the electric conductivity became 50 μS/cm, thereby obtaining a photo-functional slurry. The pH of the obtained photo-functional slurry was measured (D-22, manufactured by Horiba Ltd.) and found to be 8.5.

A part of this slurry was sampled and the solid concentration thereof was measured by a dry constant weight method and found to be 10% by mass. Then, the obtained powder was subjected to an analysis by FT-IR (FT-IR 1650, manufactured by Perkin Elmer Inc.), as a result, the absorption of metaphosphoric acid was observed. The dried powder was analyzed by ICP (ICPS-100V, manufactured by Shimadzu Corporation) and then, it was found that 5,000 ppm of Ca and 12,000 ppm of phosphorous were present. Furthermore, the primary particle size was determined by

measuring the BET specific surface area (using Flow Sorb II 2300, manufactured by Shimadzu Corporation) and found to be 0.015 μm.

[0032]

(Production of Coating)

Pure water was added to the photo-functional slurry obtained above to dilute the slurry to a concentration of 0.5% by mass in terms of powder. To this slurry, a water dispersion-type urethane resin (VONDIC1040NS, produced by Dai-Nippon Ink & Chemicals, Inc.) was added to have a urethane resin concentration of 70% by mass based on the powder, thereby obtaining a coating agent containing a photo-functional powder and a urethane resin.

Subsequently, a polyester nonwoven fabric (6 denier, produced by Takayasu) was impregnated with the obtained coating agent, taken out, squeezed by rollers and dried at 80°C for 2 hours to obtain a polyester nonwoven fabric having supported thereon a photo-functional powder.

[0033]

(Evaluation of Photocatalytic Activity)

10 g of the polyester nonwoven fabric obtained above was placed in a 5 L-volume Tedler bag (manufactured by Gastec Corporation) and 60 ppm of hydrogen sulfide was sealed thereinto. Subsequently, light was irradiated on the sample using Black Light (FL205.BL, 20 W, manufactured by

Hitachi Ltd.) such as that 0.25 mW/cm² of ultraviolet ray at 365 nm was emitted. After 2 hours, the concentration of hydrogen sulfide was measured by a detector tube (No. 4LL, manufactured by Gastec Corporation). The concentration of hydrogen sulfide after 2 hours was scarcely detected.

[0034]

(Weather Resistance Test)

The polyester nonwoven fabric prepared above was exposed to light of 50 mW/cm² from a fade meter (SUNSET CPS+, manufactured by Heraeus) and after 24 hours, the coloring of the fiber was examined but no coloring was observed. These results are shown in Table 1.

[0035]

Example 2:

The coating agent containing photo-functional powder and urethane resin obtained in Example 1 was coated on one surface of a 100-µm polyethylene terephthalate film (Lumilar T, produced by Toray Industries, Inc.) using a 25-µm applicator and then dried at 80°C for 2 hours to obtain a polyethylene terephthalate having supported thereon a photo-functional powder.

The obtained polyethylene terephthalate film was cut into 600 cm² and using this film, the evaluation of photocatalytic activity in an oxidation reaction of hydrogen sulfide and the weather resistance test were

performed in the same manner as in Example 1.

Also, the obtained photo-functional powder-supported polyethylene terephthalate film was subjected to a measurement of transmittance using a spectrophotometer (UV-2400PC, manufactured by Shimadzu Corporation), as a result, the transmittance was 5% at 360 nm and 98% at 550 nm. These results are shown in Table 1.

[0036]

Example 3:

A part of the photo-functional slurry obtained in Example 1 was dried by a medium fluidized drier (Slurry Drier, manufactured by Okawara Mfg. Co., Ltd.) to obtain 5 kg of photo-functional powder having a Ca-containing condensed phosphate on the surface of titanium dioxide fine particles.

(Production of High-Density Polyethylene Masterbatch)

20 Parts by mass of the obtained photo-functional powder, 2 parts by mass of zinc stearate (Zinc Stearate S, produced by NOF Corporation) and 78 parts by mass of high-density polyethylene (Jrex F6200FD, produced by Japan Polyolefins Co., Ltd.) were melt-kneaded at 170°C (residence time: about 3 minutes) using a twin-screw extruder (Model PCM30, manufactured by Ikegai Iron Works, Ltd.) and the kneaded product was pelletized to form 20 kg of a high-density polyethylene masterbatch (compound) containing 20%

of cylindrical photo-functional fine particles having a diameter of 2 to 3 mmϕ, a length of 3 to 5 mm and a weight of 0.01 to 0.02 g.

[0037]

(Spinning)

In a V-type blender (surface of titanium dioxide fine particle, RKI-40, manufactured by Ikemoto Scientific Technology Co., Ltd.), 10 kg of the photo-functional powder-containing high-density polyethylene masterbatch (compound) obtained above and 10 kg of high-density polyethylene (Jrex F6200FD, produced by Japan Polyolefins Co., Ltd.) were mixed for 10 minutes to obtain mixed pellets.

The obtained mixed pellet and a polyester resin pellet (FM-OK, produced by Teijin Limited) each was charged into a melt extrusion spinning machine (Polymer-Maid 5, manufactured by Chuo Kagaku Kikai Seisakusho) and spun at a pack temperature of 300°C to produce 35 kg of 12-denier fiber having a core-sheath structure of photocatalyst-containing high-density polyethylene (sheath)/polyester resin (core) such that the mass ratio of the photo-functional powder-containing high-density polyethylene to the polyester resin was 1:1.

Using 10 g of the obtained fiber, the evaluation of photocatalytic activity and the weather resistance test

were performed in the same manner as in Example 1. The results are shown in Table 1.

[0038]

Example 4:

A coating agent containing a photo-functional powder and a urethane resin was produced in the same manner as in Example 1 except for using 300 g of magnesium chloride (for food addition, produced by Naikai Salt Industries Co., Ltd.) in place of 200 g of calcium chloride described in Example 1. The produced coating agent was coated on a polyethylene terephthalate film in the same manner as in Example 2 to obtain a polyethylene terephthalate film having supported thereon a photo-functional powder and this film was subjected to the evaluation of evaluation of photocatalytic activity, the weather resistance test and the measurement of transmittance. The results are shown in Table 1.

[0039]

Example 5:

A coating agent containing a photo-functional powder and a urethane resin was produced in the same manner as in Example 1 except for using 2.3 kg of sodium polyphosphate (for food addition, produced by Taihei Chemical Industrial Co., Ltd.) in place of 1 kg of the sodium metaphosphate described in Example 1. The produced coating agent was

coated on a polyethylene terephthalate film in the same manner as in Example 2 to obtain a polyethylene terephthalate film having supported thereon a photo-functional powder, shown in the results of Table 1.

This photo-functional powder-supported polyethylene terephthalate film was then subjected to the evaluation of photocatalytic activity, the weather resistance test and the measurement of transmittance. The results obtained are shown in Table 1.

[0040]

Example 6:

A polyethylene terephthalate film having supported thereon a photo-functional powder was obtained in the same manner as in Example 5 except for using 1.5 kg of sodium ultraphosphate (for food addition, produced by Taihei Chemical Industrial Co., Ltd.) in place of 2.3 kg of sodium polyphosphate described in Example 5. This photo-functional powder-supported polyethylene terephthalate film was then subjected to the evaluation of photocatalytic activity, the weather resistance test and the measurement of transmittance. The results obtained are shown in Table 1.

[0041]

Comparative Example 1:

A coating agent containing a urethane resin was produced in the same manner as in Example 1 using the

brookite-type titanium dioxide described in Example 1. The obtained coating agent was coated on a polyethylene terephthalate film in the same manner as in Example 2 to obtain a polyethylene terephthalate film having supported thereon titanium dioxide. This film was then subjected to the evaluation of photocatalytic activity, the weather resistance test and the measurement of transmittance. The results obtained are shown in Table 1.

[0042]

Comparative Example 2:

To 200 L of pure water, 10 kg of a commercially available pigment-use anatase (A100, produced by Ishihara Sangyo Kaisha Ltd.) having a particle size of 0.18 μm was added and further, 1 kg of sodium metaphosphate (for food addition, produced by Taihei Chemical Industrial Co., Ltd.) was added thereto. The obtained solution was thoroughly stirred until these were dispersed.

Subsequently, 200 g of calcium chloride (for food addition, produced by Tokuyama Corp.) was added to 2,000 L of pure water previously weighed and the mixture was stirred by a lab stirrer to prepare a calcium chloride solution. The obtained titanium dioxide slurry containing sodium metaphosphate and calcium chloride solution were mixed and kept at 40°C for 4 hours. At this time, the electric conductivity was 10,000 μS/cm. The obtained slurry

was cleaned by filtration through a rotary filter press (manufactured by Kotobuki Engineering & Manufacturing Co., Ltd.) and then thoroughly washed until the electric conductivity became 50 μS/cm. Subsequently, a part of the obtained slurry was sampled and the solid concentration was measured by a dry constant weight method and found to be 10% by mass. The obtained powder was then analyzed by FT-IR (FT-IR 1650, manufactured by Perkin Elmer Inc.), as a result, absorption of metaphosphoric acid was observed. The dried powder was analyzed by ICP (ICPS-100V, manufactured by Shimadzu Corporation) and then, it was found that 2,000 ppm of Ca and 8,000 ppm of phosphorus were present.

Using the obtained slurry, a coating agent containing a urethane resin was produced according to the method described in Example 1. This coating agent was coated on a polyethylene terephthalate film in the same manner as in Example 2 to obtain a polyethylene terephthalate film having supported thereon a photo-functional powder. This film was then subjected to the evaluation of photocatalytic activity, the weather resistance test and the measurement of transmittance. The results obtained are shown in Table 1.

[0043]

Comparative Example 3:

The water-soluble urethane resin described in Example 1 was dissolved in pure water to a concentration of 0.35%.

The obtained coating was then coated on the polyethylene terephthalate film described in Example 2 to obtain a film. Subsequently, this film was subjected to the evaluation of photocatalytic activity, the weather resistance test and the measurement of transmittance. The results obtained are shown in Table 1.

[0044]

[Table 1]

Table 1

	Particle Size of Titanium Dioxide	Condensed Phosphoric Acid	Alkaline Earth Metal	Use Form
Example 1	0.015 μm	metaphosphoric acid	Ca	coating on nonwoven fabric
Example 2	0.015 μm	metaphosphoric acid	Ca	coating on film
Example 3	0.015 μm	metaphosphoric acid	Ca	kneading into fiber
Example 4	0.015 μm	metaphosphoric acid	Mg	coating on film
Example 5	0.015 μm	polyphosphoric acid	Ca	coating on film
Example 6	0.015 μm	ultraphosphoric acid	Ca	coating on film
Comparative Example 1	0.015 μm	-	-	coating on film
Comparative Example 2	0.200 μm	metaphosphoric acid	Ca	coating on film
Comparative Example 3	-	-	-	coating on film

[0045]

[Table 2]

Table 1 (continued)

	Residual ratio	Weather Resistance Test	Transmittance at 360 nm	Transmittance at 550 nm
Example 1	0%	no coloring	-	-
Example 2	25%	no coloring	5%	98%
Example 3	0%	no coloring	-	-
Example 4	30%	no coloring	4%	97%
Example 5	32%	no coloring	6%	96%
Example 6	28%	no coloring	5%	95%
Comparative Example 1	20%	colored	3%	98%
Comparative Example 2	98%	no coloring	2%	3%
Comparative Example 3	100%	no coloring	96%	99%